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Study on the high-temperature tribological performance of biodegradable ultrafine β-tricalcium phosphate reinforced barium complex grease

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Lubricating additives are essential for enhancing the tribological properties of grease. The development of low-cost lubricant additives with excellent biodegradability is expected to be the prevailing trend for future advancements. In this study, biodegradable ultrafine β-tricalcium phosphate (β-TCP) was utilized to enhance the friction reduction, anti-wear and extreme pressure properties of barium complex greases at high temperatures. At 150 °C and a load of 150 N, compared to the base grease, the average friction coefficient (AFC) of barium complex grease with 4.5% β-TCP was reduced by 21.82%. Meanwhile, the wear volume was reduced by 88.43%. Moreover, the extreme pressure properties of the barium complex grease were increased by 3.75 times. The lubrication mechanism of β-TCP is the formation of a protective film of P and Ca compounds on the surface of the friction partner.

1 Introduction

Grease is an important lubricating material widely used to reduce friction and wear in mechanical equipment components.[1,2] Grease is a lubricating material with non-Newtonian fluid properties consisting of a base oil, thickener and additives.[3,4] Lubricating additives are essential for enhancing the tribological properties of grease.[5,6] With advancements in machinery and equipment, mechanical components are often subjected to high temperatures, heavy loads, and other demanding conditions.[7–9] These challenges require grease to provide reliable lubrication for moving parts under harsh operating environments.[7,9] High-temperature lubricating additives play an important role in maintaining effective lubrication in such conditions.[9–11] Therefore, the development of additives that exhibit superior high-temperature lubrication performance is vital for enhancing the overall high-temperature lubrication capabilities of grease.

In recent decades, a lot of compounds have been investigated as high-temperature additives for greases. Zhu *et al.* explored the use of fluorinated diphenyl phosphate esters to enhance friction reduction and anti-wear properties of polyurea greases at 100 °C.[12] Similarly, phosphate ionic liquids and molybdenum dialkyl dithiophosphate have been shown to enhance the tribological properties of lithium complex greases and polyurea greases under high-temperature conditions.[11,13] While these additives enhance the high-temperature tribological performance of lubricating greases, their poor biodegradability poses significant environmental challenges. Solid lubrication additives have emerged as a key focus in the development of high-temperature grease additives due to their excellent thermal stability. Wang *et al.* studied the influence of micron-scale multi-layered graphene on the tribological properties of polyurea lubricating grease, demonstrating improved performance at 100 °C.[14] Zhang *et al.* used micron-scale Ti_3C_2 MXenes to enhance the tribological properties of lithium grease at 120 °C, though performance significantly deteriorated when the temperature at 160 °C. Additionally,[15] Zhang *et al.* examined the tribological properties of WS_2 nanoparticles as an additive in calcium sulfonate complex–polyurea grease, finding that the inclusion of WS_2 nanoparticles yielded optimal friction reduction and anti-wear performance at 150 °C.[16] While solid additives can improve the tribological performance of lubricating greases in high-temperature environments, their preparation processes are often complex and costly. Furthermore, some preparation methods involve the use of strong acids, raising concerns about environmental sustainability. These challenges hinder the widespread adoption of solid additives in lubricating greases. As environmental regulations become increasingly stringent, the development of low-cost lubricant additives with good biodegradability is expected to be the prevailing trend for future advancements.[17]

Inorganic phosphates are licensed by the U.S. Food and Drug Administration (FDA) for use in drug excipients.[18] β-Tricalcium phosphate (β-TCP) exhibits excellent biodegradability, biocompatibility, and thermal stability and has been

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successfully applied for many years in bioengineering, food, and pharmaceutical industries.[19,20] Building on the molecular structure and composition of existing lubricant additives, it is hypothesized that ultrafine β-TCP holds potential as a high-temperature lubricant additive for greases. However, to date, ultrafine β-TCP has not been studied as a high temperature lubricant additive for greases.

Barium complex greases have good high temperature performance and water resistance, widely used in metallurgy, bearings and other industries.[21] In this study, ultrafine β-TCP was prepared using the co-precipitation process, and its microstructure and composition were characterized through SEM, infrared spectroscopy, and X-ray diffraction (XRD). The friction reduction, anti-wear, and extreme pressure properties of ultrafine β-TCP as a high-temperature lubricant additive for barium complex greases were thoroughly investigated. The lubrication mechanism was analyzed based on surface examinations of the friction partners. This study offers a novel approach for developing high-temperature grease additives with excellent biodegradability.

2 Materials and methods

2.1 Materials

Calcium dinitrate tetrahydrate (CDE) and diammonium hydrogenphosphate (DH)were procured from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Ammonia and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Barium complex grease was supplied by Qingdao Lubemater Lubrication Materials Technology Co., Ltd.

2.2 Synthesis of ultrafine β-TCP and preparation of grease samples

Ultrafine β-TCP was produced by co-precipitation process.[22,23] First, CDE and DH were dissolved in ethanol and deionized water to form solutions, respectively. Then the CDE solution was added dropwise to the DH solution at 40 °C with thorough stirring, and the pH of the mixed solution was maintained at about 7 by the addition of ammonia during precipitation. After its precipitation was complete, the solution was placed for 24 h in a water bath at 40 °C. The precipitate was first washed three times with anhydrous ethanol. It was then washed three times with deionised water. The precipitate was dried at 100 °C for 24 h in a vacuum oven. Finally, the dried powder was calcined at 800 °C for 2 h to obtain ultrafine β-TCP.

The grease containing ultrafine β-TCP was prepared as follows: ultrafine β-TCP is added to the barium complex grease according to different mass fractions. First, it is mixed using a mixer (SpeedMixer, FlackTek) at 2000 rpm for 10 minutes, and then ground three times with a precision three-roll grinder. Different grease samples were obtained. The samples were labelled as base grease, 1.5% β-TCP, 3.0% β-TCP, 4.5% β-TCP, and 6.0% β-TCP according to the mass fraction. The physicochemical properties of the grease samples are shown in Table 1.

2.3 Characterization

The microscopic morphology of ultrafine β-TCP was characterized using a field emission scanning electron microscope (SEM, JSM-7610F, JEOL). The infrared spectra of the β-TCP were tested using a Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker). The X-ray diffraction (XRD, Bruker D8, Bruker) was carried out to investigate crystalline structure of the β-TCP (2θ range of 10–70°).

2.4 Tribological test

The tribological properties of the barium complex grease were studied using an SRV tester (SRV-V, Optimol). The steel ball (diameter: 10 mm) and steel disk (diameter: 24 mm, thickness: 7.9 mm) were friction partners. The material of the friction pair was bearing AISI 52100 steel with an of 60 ± 2. The test parameters are referred to existing ref. 15, 16 and 24. All tribological tests were conducted with an amplitude of 1 mm and a frequency of 25 Hz. The applied test loads were 100 N, 150 N, and 200 N, while the test temperatures were 100 °C, 150 °C, and 170 °C. The test periods were 30 min. The extreme pressure properties of the barium complex grease were assessed under the test conditions: a temperature of 150 °C, a stroke of 1 mm, and a frequency of 25 Hz. A load ramp test was performed by increasing the load by 50 N every 2 min.

A field emission SEM (JSM-7610F, JEOL) with energy dispersive spectroscopy (EDS) was utilized to characterize the morphology and element composition of wear scars. A optical 3D profilometer (UP-Sigma, Rtec) was utilized to analyze the parameters of the wear scars. This includes wear volume, 3D morphology and cross-sectional depth of wear scar. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific) was employed to characterize the chemical composition of the worn surface.

3 Results and discussion

3.1 Characterization of ultrafine β-TCP

The composition and structure of ultrafine β-TCP were analyzed using FTIR and XRD. The FTIR spectrum (Fig. 1a) clearly show the characteristic absorption peaks of ultrafine β-TCP. The

Table 1 Physicochemical properties of the grease samples

Samples	Base grease	1.5% β-TCP	3.0% β-TCP	4.5% β-TCP	6.0% β-TCP	Test method
NLGI grade	2	2	2	2	2	
Penetration (0.1 mm)	284	277	272	270	269	GB/T 269
Dropping point (°C)	305	309	311	312	314	GB/T 3498
Oil separation (%)	1.26	1.13	1.12	0.97	0.92	NB/SH/T 0324

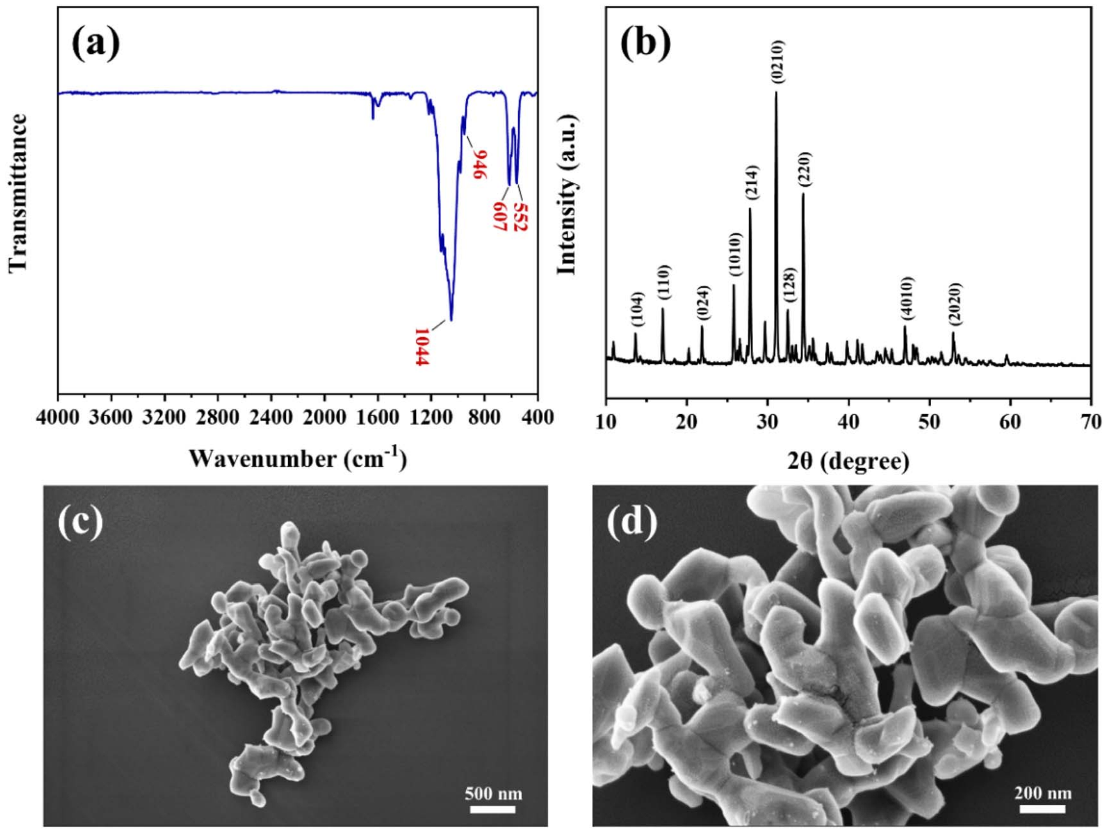

Fig. 1 Structural and morphological characterization of ultrafine β-TCP. (a) FTIR spectrum, (b) XRD pattern, and (c and d) SEM images.

PO_4^{3-} stretching vibration peaks were observed at 552, 607, 946 and 1044 cm^{-1}.[25] The XRD pattern (Fig. 1b) of the prepared ultrafine β-TCP, exhibiting narrow and strong diffraction peaks, was in agreement with the standard reference (JCPDS card no. 09-0169). These results confirm that the prepared calcium phosphate is of the β-crystalline type and is well crystallized. The microscopic morphology of ultrafine β-TCP was examined using SEM (Fig. 1c and d). The images revealed that ultrafine β-TCP exhibits an irregular rod-like structure with a length of ~1 μm. These findings demonstrate the successful synthesis of β-crystalline calcium phosphate.

3.2 Tribological properties

The friction reduction and anti-wear properties of barium complex greases with different mass fractions of β-TCP were evaluated at 150 °C using an SRV tester. The optimum mass fraction of β-TCP in the barium complex grease was determined. The test loads were 100 N, 150 N, and 200 N (Fig. 2). The effect of β-TCP mass fractions on the coefficient of friction for barium complex grease were shown in Fig. 2(a)–(c). The highest friction coefficient curve was observed for base grease. Adding β-TCP significantly reduced the friction coefficient of the grease, and the friction curve decreased progressively with increasing β-TCP mass fraction. The sample with 4.5% β-TCP exhibited the lowest friction curve, while the friction coefficient of the 6.0% β-TCP sample slightly increased compared to the 4.5% sample. The variation in the friction coefficient was confirmed by the AFC results in Fig. 2(d). Similarly, the wear volume trends shown in Fig. 2(e) were consistent with those of the AFC. The sample with 4.5% β-TCP had the smallest wear volume. Therefore, the optimal mass fraction of β-TCP in barium complex grease was determined to be 4.5%. Compared to the base grease, the AFC for the 4.5% β-TCP sample decreased by 18.86%, 21.82%. and 18.18% at 100 N, 150 N and 200 N, respectively. Correspondingly, the wear volume was reduced by 85.26%, 88.43% and 83.33%. The detailed test results for the AFC and wear volume were shown in Table 2. The experimental results show that β-TCP significantly enhances the friction reduction and anti-wear performance of barium complex grease. The optimum mass fraction in the barium complex grease was 4.5%. This is because when the mass fraction of β-TCP is low (1.5%, 3.0%), it is difficult to form an adequate protective film on the surface of the friction pair, so the friction reduction and anti-wear performance are poor. Conversely, at higher mass fractions (6.0%), excess β-TCP agglomerates, weakening its friction reduction and anti-wear capabilities.[26,27] Additionally, under a load of 150 N, the barium complex grease with 4.5% β-TCP exhibited the optimum friction reduction and anti-wear performance.

Temperature is an essential factor affecting the lubricating performance of grease.[15] Lubrication additives are essential for enhancing grease performance under high-temperature operating conditions. The effect of β-TCP on the tribological properties of barium complex grease was examined at different

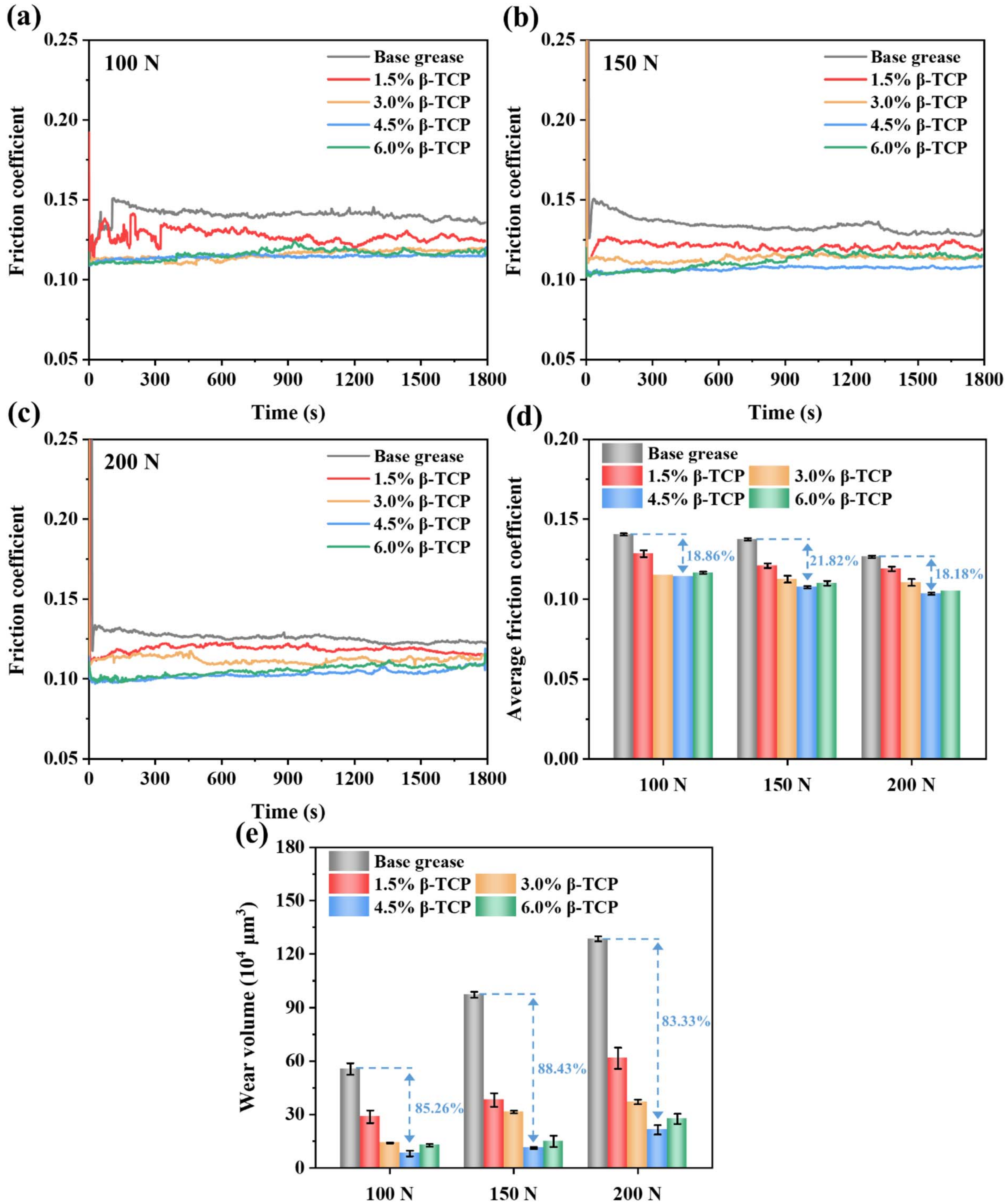

Fig. 2 Friction coefficient curves (a) 100 N, (b) 150 N and (c) 200 N, AFC (d) and wear volume (e) of barium complex grease containing different mass fractions of β-TCP under loads of 100 N, 150 N and 200 N (temperature: 150 °C).

temperatures. The test temperatures were 100 °C, 150 °C and 170 °C, as shown in Fig. 3. From Fig. 3(a), it can be observed that, at the same temperature, the AFC of the 4.5% β-TCP sample was lower than that of pure barium complex grease. Compared to the pure barium complex grease., the AFC of the 4.5% β-TCP sample decreased by 9.92%, 21.82% and 20.21% at 100 °C, 150 °C and 170 °C, respectively. β-TCP dramatically enhanced the friction reduction performance of the barium complex grease. The results of the wear volume tests as shown in Fig. 3(b). Compared to the base grease, the wear volume of the 4.5% β-TCP sample was reduced by 85.97%, 88.43%, and 70.92%, respectively. The addition of β-TCP significantly enhanced the anti-wear performance of the barium complex grease. Notably, at 150 °C, the reduction in the AFC and wear

Table 2 Tribological performance test results

Loading (N)	Grease	AFC	Wear volume (10^4 μm^3)
100	Base grease	0.1405	55.48
	1.5% β-TCP	0.1285	28.68
	3.0% β-TCP	0.1150	14.16
	4.5% β-TCP	0.1140	8.18
	6.0% β-TCP	0.1165	12.78
150	Base grease	0.1375	97.28
	1.5% β-TCP	0.1210	38.11
	3.0% β-TCP	0.1125	31.38
	4.5% β-TCP	0.1075	11.26
	6.0% β-TCP	0.1100	15.03
200	Base grease	0.1265	128.52
	1.5% β-TCP	0.1190	61.59
	3.0% β-TCP	0.1105	37.01
	4.5% β-TCP	0.1035	21.42
	6.0% β-TCP	0.1050	27.44

volume was the highest, demonstrating optimal friction reduction and anti-wear performance. In conclusion, β-TCP significantly improved the friction reduction and anti-wear properties of barium complex grease at high temperatures. This enhancement occurs because β-TCP forms a protective film on the surface of the friction partners, effectively preventing direct contact between them, reducing friction and wear, and further improving the overall friction reduction and anti-wear performance of the barium complex grease.

The extreme pressure performance is an important property of lubricating grease. High extreme pressure performance indicates greater load carrying capacity and enhanced protection against seizure in tribological pairs. To study the influence of β-TCP on the load carrying capacity of barium complex grease, the extreme pressure performance of pure barium complex grease and 4.5% β-TCP was evaluated using a load ramp test, as shown in Fig. 4. When the load increased to 200 N, the friction coefficient of the base grease rose rapidly and then decreased sharply. As the load continued to rise from 400 N to 450 N, the friction coefficient of pure barium complex grease increased dramatically, fluctuated intensely, and seizure phenomena occurred in the tribological pair; this indicates that the maximum load capacity of the base grease is 400 N. Interestingly, the friction coefficient of the 4.5% β-TCP sample is significantly lower than that of the base grease, with slight fluctuations observed within the test load range of 400 N to 1500 N (test duration: 600–3600 s). These fluctuations are attributed to instantaneous changes in friction caused by load increases. When the load exceeds 1500 N, the friction coefficient of the 4.5% β-TCP sample fluctuates drastically, leading to seizure in the friction pair. The maximum load capacity of the 4.5% β-TCP sample is 1500 N. These results demonstrate that β-TCP significantly improves the load carrying capacity of barium complex grease. This improvement can be attributed to the lubricant film formed by β-TCP, which prevents direct contact between friction partners and thus reduces the risk of seizure.[28]

3.3 Worn surface analyses

To further analyze the influence of β-TCP on the anti-wear performance of barium complex grease, the microscopic morphology of wear scars on steel disks of barium complex grease with varying mass fractions of β-TCP was examined using SEM. As shown in Fig. 5, the wear scar edges of the base grease exhibit irregular scratches, with deep grooves and pits indicating severe surface wear. In the sample containing 1.5% β-TCP, the pits are reduced, though deeper grooves remain. As the β-TCP concentration increases, the irregular scratches on both sides of the wear scar edges diminish, grooves become progressively shallower, and pits decrease significantly. The wear scar surface of the 4.5% β-TCP sample is the smoothest, with the shallowest grooves, showing the best anti-wear performance. However, when the mass fraction of β-TCP reaches 6.0%, the grooves deepen slightly; this occurs because higher β-TCP concentrations can lead to agglomeration during friction, resulting in abrasive wear and reduced lubrication performance. These findings align with the wear volume test results.

The 3D morphology and cross-sectional profiles of wear scars of barium complex grease samples with varying β-TCP mass fractions were analyzed using a 3D profile tester. As shown in Fig. 6, the wear scar of the base grease is deep, with a maximum depth of 4.73 μm and prominent valley peaks. The edges of the wear scar show severe scuffing. These results indicate that

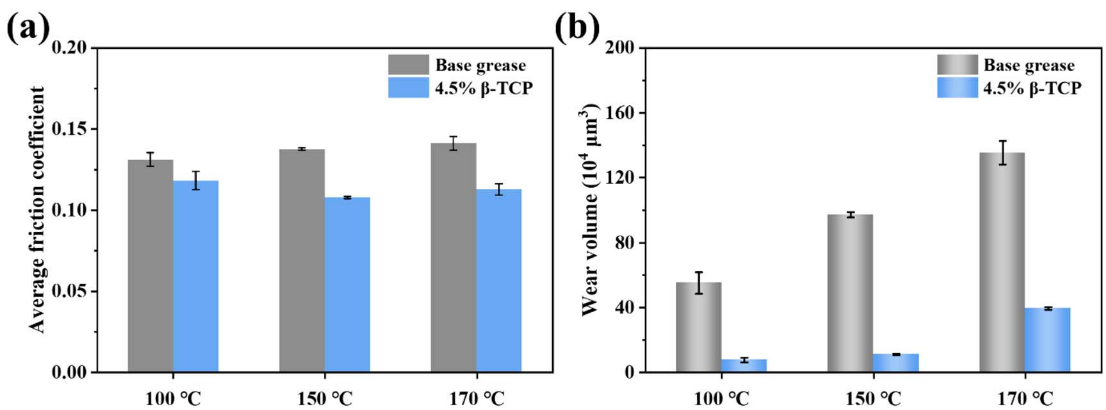

Fig. 3 AFC (a) and wear volume (b) of base grease and 4.5% β-TCP at 100 °C, 150 °C and 170 °C (load: 150 N).

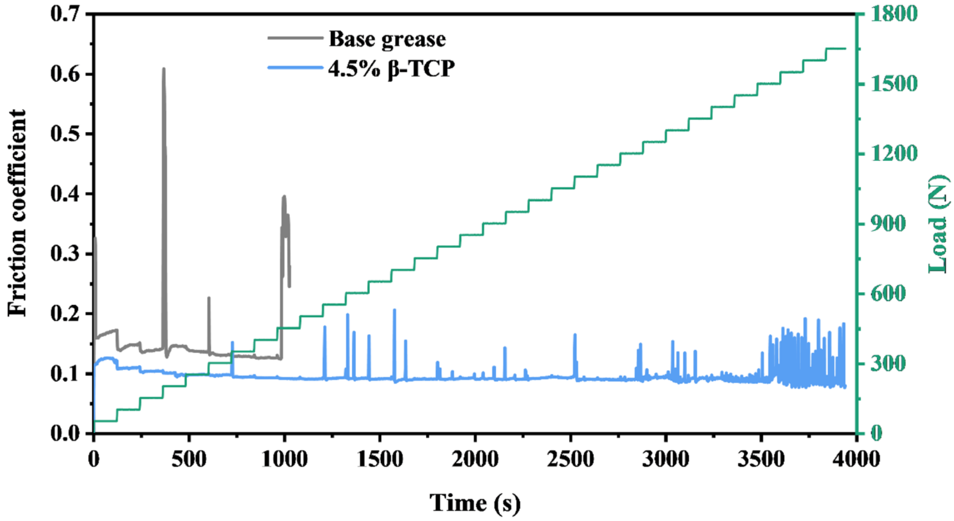

Fig. 4 Extreme pressure performance of base grease and 4.5% β-TCP (temperature: 150 °C; load: increased by 50 N every 2 min).

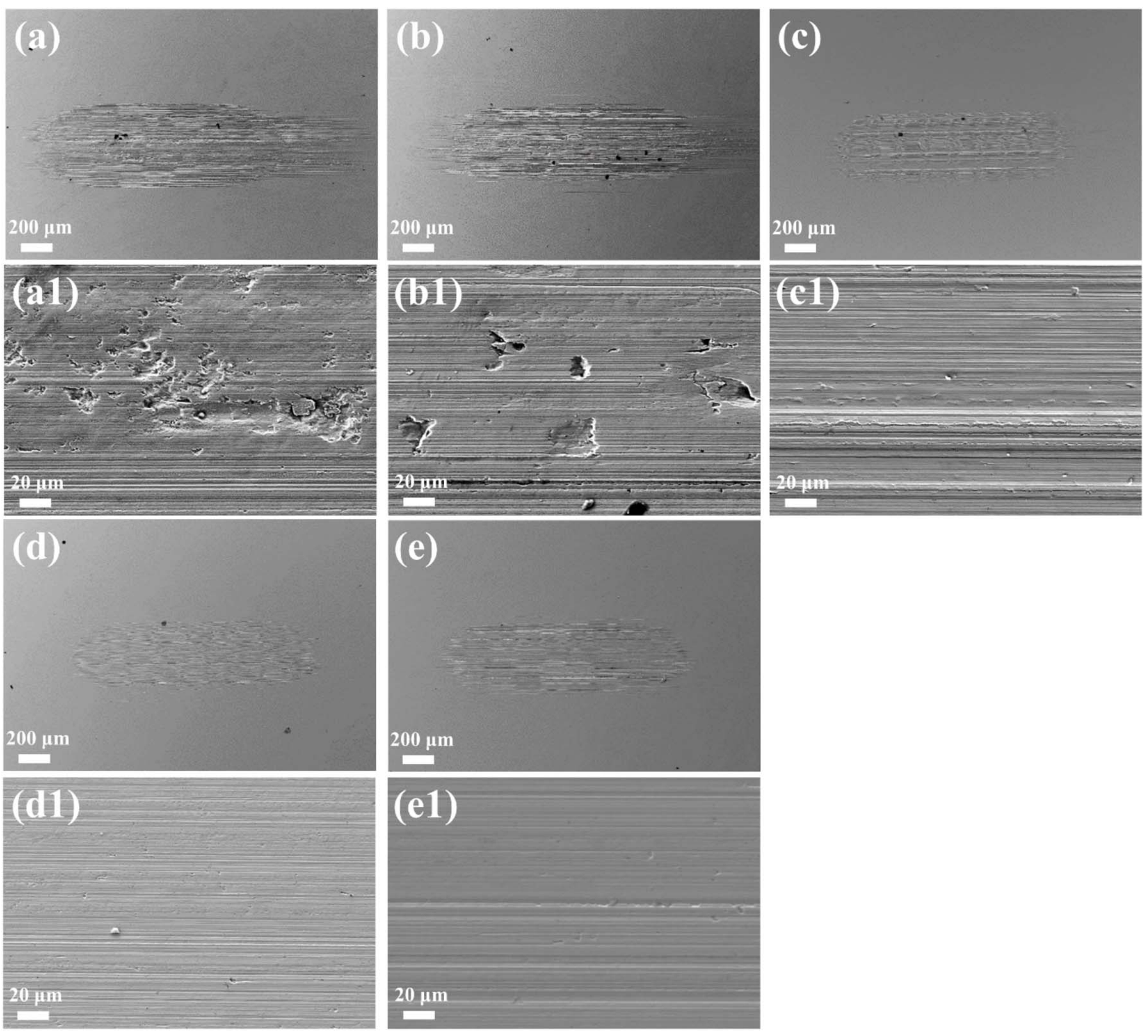

Fig. 5 SEM images of worn surface on test disks lubricated with barium complex grease containing varying mass fractions of β-TCP at 150 °C under a load of 150 N. (a and a1) Base grease; (b and b1) 1.5% β-TCP; (c and c1) 3.0% β-TCP; (d nad d1) 4.5% β-TCP; (e and e1) 6.0% β-TCP.

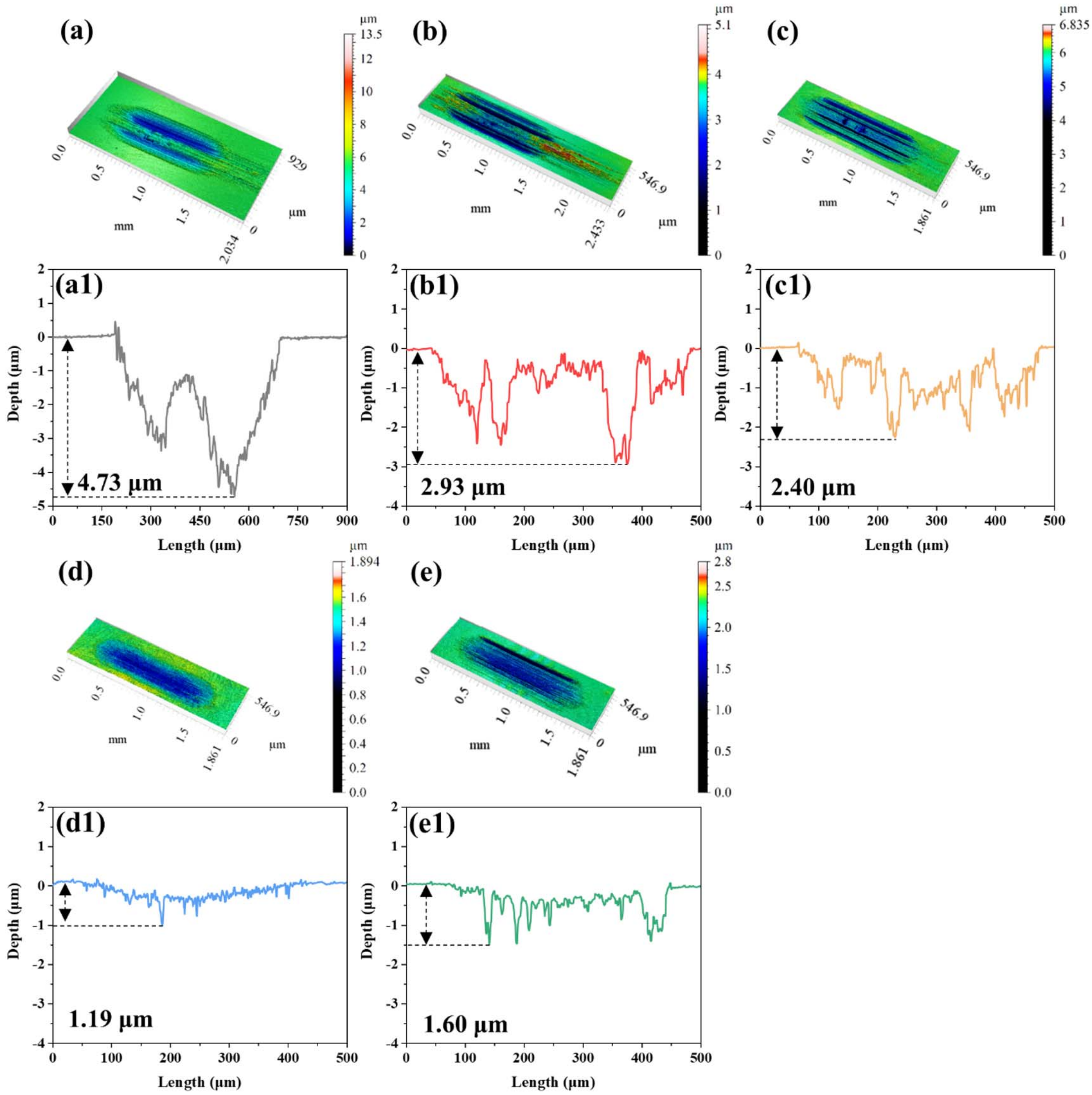

Fig. 6 3D morphology (a–e) and cross-sectional profiles (a1–e1) of wear scars on test disks lubricated with barium complex grease containing varying mass fractions of β-TCP at 150 °C under a load of 150 N.

severe wear has occurred on the surface of the disks. In comparison, the wear scar depths of the 1.5% β-TCP and 3.0% β-TCP samples are shallower, with reduced valley peak fluctuations. The maximum wear scar depths are 2.93 μm and 2.40 μm, respectively. The 4.5% β-TCP sample displays the shallowest wear scar and the smoothest surface. The maximum depth is 1.19 μm. The scuffing on the edges of the wear scar disappeared. This indicates a significant reduction in wear. However, with a further increase to 6.0% β-TCP, the wear scar depth slightly increases. In summary, the 4.5% β-TCP sample exhibits the shallowest wear scar. The surface is also the smoothest. This result aligns with the SEM findings in Fig. 5, further confirming that β-TCP significantly improves the anti-wear performance of barium complex grease.

3.4 Lubrication mechanism

To investigate the lubrication mechanism by which β-TCP enhances the tribological performance of barium complex grease, the elemental distribution on the worn surface of disks lubricated with 4.5% β-TCP was analyzed using EDS. As shown in Fig. 7, the presence of P and Ca elements, originating from β-TCP, was clearly detected; this indicates that β-TCP forms a protective film on the wear scar surface. During friction, this protective film effectively minimizes direct contact between friction partners, thereby significantly improving the tribological properties of barium complex grease.[26]

To further analyze the mechanism by which β-TCP-reinforces barium complex grease, the elemental composition and valence states of the wear scar surface were investigated using XPS. The high-resolution XPS spectra of Fe 2p, O 1s, P 2p, and Ca 2p as shown in Fig. 8. The fitted spectrum of Fe 2p is shown in Fig. 8(a). The Fe 2p spectra could be deconvoluted into three peaks at 710.3 eV, 712.8 eV and 724 eV. These three peaks correspond to FeO, $FePO_4$, and Fe_2O_3, respectively.[29–31] After fitting the O 1 s spectrum, it could be deconvoluted into two absorption peaks. The first, at

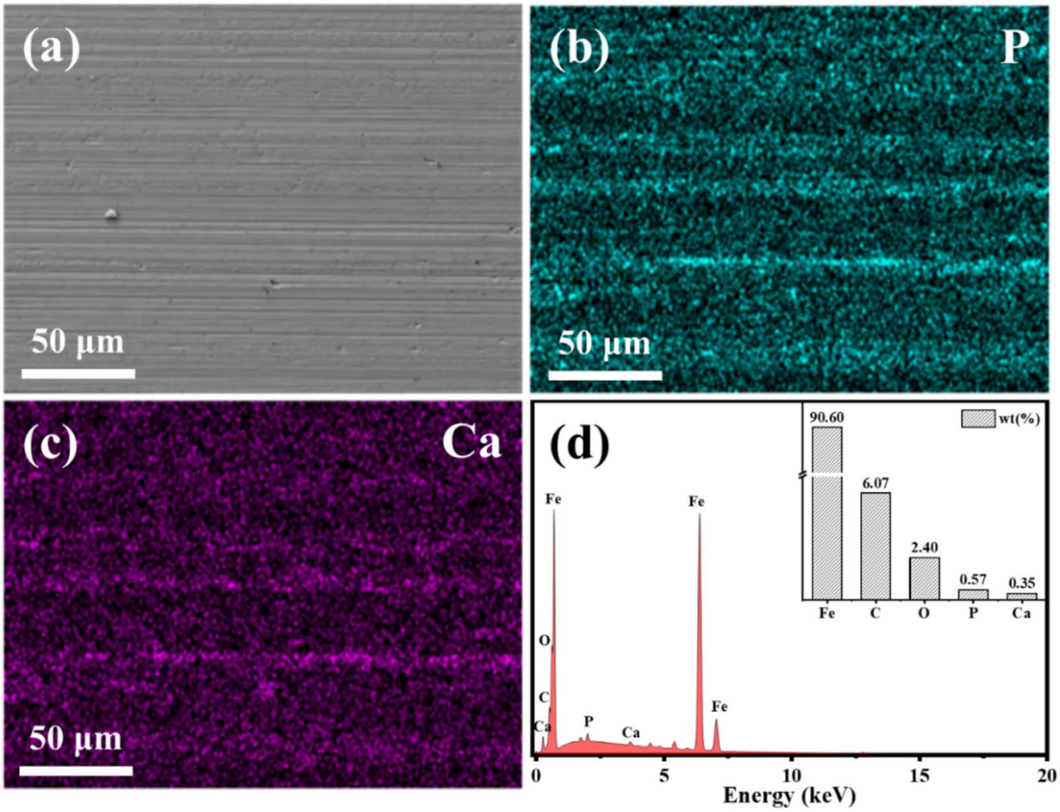

Fig. 7 SEM images (a) and EDS results (b–d) of worn surface on disks lubricated with 4.5% β-TCP at 150 °C under a load of 150 N.

530.2 eV, corresponds to Fe_2O_3, while the second, at 531.7 eV, is attributed to phosphates, such as $FePO_4$, $Fe_3(PO_4)_2$, and $Ca_3(PO_4)_2$.[32–34] These findings align with the Fe 2p analysis. The P 2p spectrum displays two absorption peaks with binding energies of 132.4 eV and 133.4 eV, corresponding to $Fe_3(PO_4)_2$ and $Ca_3(PO_4)_2$,[18,31] consistent with the O 1s results. The absorption peaks of Ca 2p at 346.8 eV and 350.5 eV are both attributable to CaO.[18,31,35,36] In conclusion, the friction film formed by β-TCP mainly consists of phosphates and oxides. These tribochemical generated compounds help to the enhanced tribological performance of β-TCP in barium complex grease at elevated temperatures.

The lubrication mechanism of β-TCP is analysed in detail (Fig. 9). The main lubrication mechanism of β-TCP-enhanced barium complex grease involves the formation of a deposition film and a chemical reaction film on the surface of friction pairs. During the initial stage of reciprocating friction, β-TCP adsorbs onto the friction pairs surfaces, forming a deposition film. This film fills microscopic recesses and scratches, reducing the shear strength during relative motion, thereby contributing to friction reduction and anti-wear performance. As reciprocating friction continues, the adsorbed β-TCP undergoes a tribochemical reaction driven by shear force and frictional heat. This reaction generates a chemical film composed of phosphates and oxides, which inhibits direct contact between surface asperities on the friction pairs. In summary, the deposition and chemical reaction films formed by β-TCP together create a lubricating layer that enhances the friction reduction, anti-wear properties, and load carrying capacity of barium complex grease. The lubricant film undergoes continuous wear and regeneration during friction. However, if the load becomes excessively high, the film may not regenerate quickly enough after being damaged, resulting in diminished friction reduction and anti-wear effects of β-TCP.[37] In addition, temperature significantly affects the formation of chemical reaction films within the lubricating film. At 100 °C, the tribochemical reaction progresses slowly, resulting in an insufficient formation of the lubricating film, which weakens the friction reduction and anti-wear properties.[16] When the temperature rises to 150 °C, the higher temperature accelerates the tribochemical reaction of β-TCP with the surface of the friction partners. Consequently, a more robust reaction film forms on the surface of the friction partners, enhancing the friction reduction and anti-wear properties.[38] However, when the temperature further increases to 170 °C, the friction and wear of the friction partners intensify. The chemical reaction film is consumed at a greater rate, and β-TCP is unable to generate a sufficient chemical reaction film in time, leading to increased friction and wear.[39] In summary, β-TCP significantly improves the friction reduction, anti-wear, and load carrying capacity of barium complex grease at high temperatures, making it a promising candidate for high-temperature lubricant additives in lubricating grease.

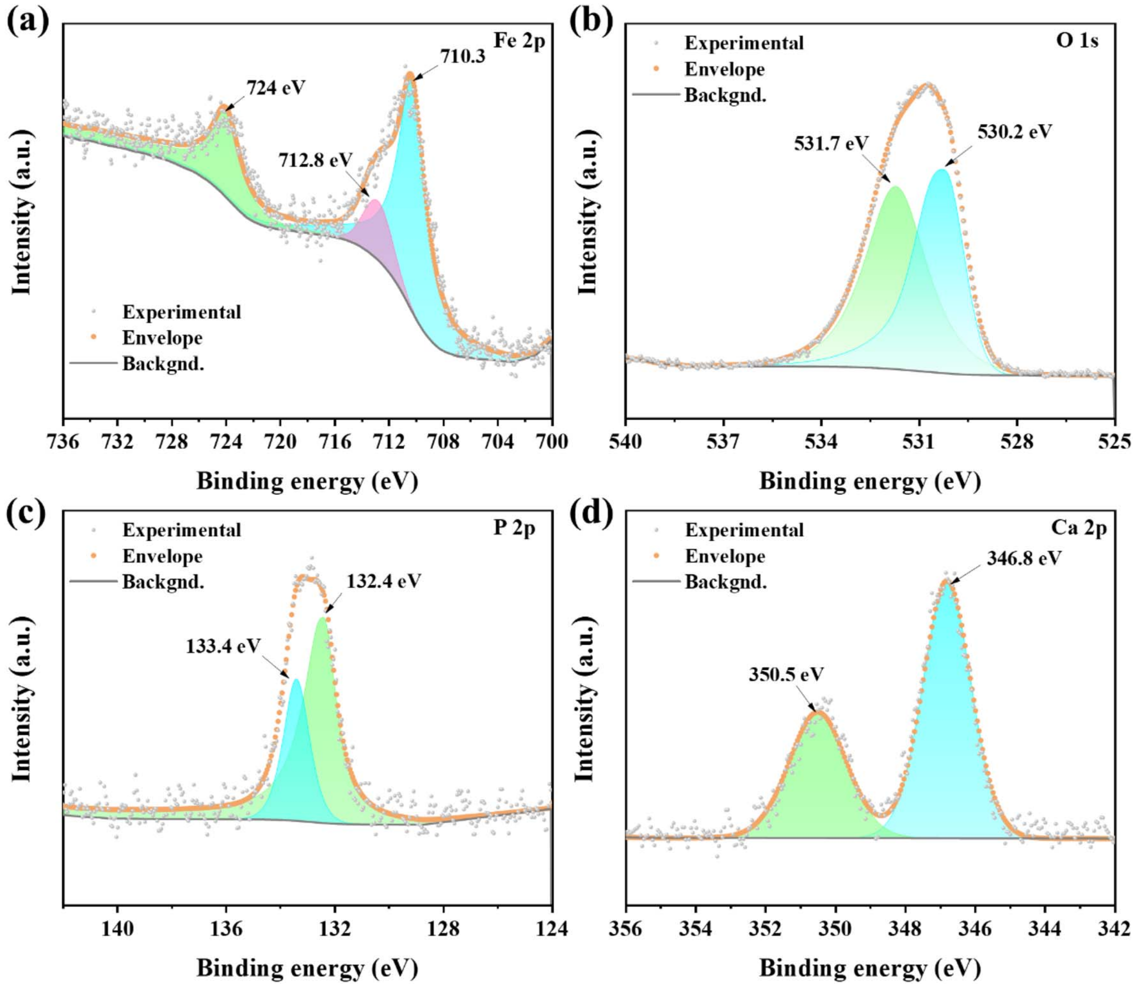

Fig. 8 XPS spectra of worn surfaces on disks lubricated with 4.5% β-TCP at 150 °C under a load of 150 N: (a) Fe 2p; (b) O 1s; (c) P 2p; (d) Ca 2p.

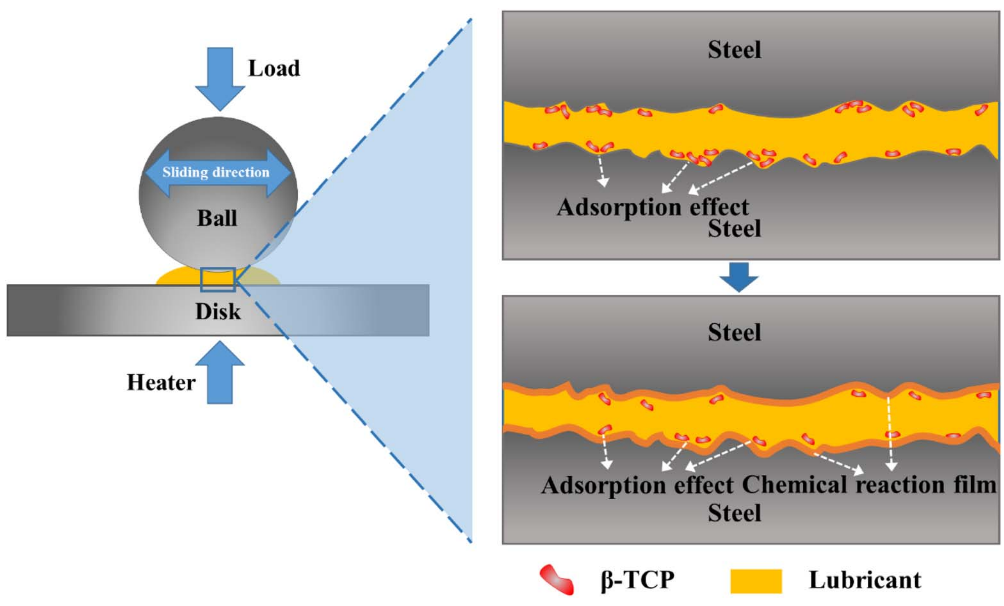

Fig. 9 Lubricating mechanism of β-TCP.

4 Conclusions

β-TCP with a well-defined crystalline structure was successfully prepared using the co-precipitation method. In our study, for the first time, investigated the feasibility of β-TCP as a high-temperature lubricant additive for barium complex grease. The lubrication mechanism of β-TCP was also analyzed. The primary finds are as follows:

(1) Tribological test results show that β-TCP significantly enhances the friction reduction and anti-wear performance of barium complex grease at high temperatures. The optimal mass fraction of β-TCP in the barium complex grease is 4.5%. At 150 °C under a load of 150 N, the AFC and wear volume of barium complex grease with 4.5% β-TCP were reduced by 21.82% and 88.43%, respectively, compared with base grease.

(2) β-TCP significantly improves the load carrying capacity of barium complex grease at High temperatures. At 150 °C, the extreme pressure properties of barium complex grease containing 4.5% β-TCP increased by 3.75 times.

(3) The superior tribological properties of β-TCP are mainly attributed to the formation of a protective film on the surface of the friction partners. This lubricating film mainly consists of a deposition film and a chemical reaction film. By preventing direct contact between the surfaces of the friction partners, the protective film displays excellent friction reduction, anti-wear, and anti-seizure properties.

Future research could explore the application of biodegradable β-TCP in other lubricants.

Data availability

All data that support the findings of this study are included in the manuscript. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Author contributions

Shuai Li: investigation, visualization, methodology, data curation, writing – original draft. Haopeng Cai: investigation, visualization, methodology, data curation, writing – review & editing. Haichao Liu: writing – review & editing. Zhuang Xu: writing – review & editing, funding acquisition, supervision, conceptualization. Wenjing Lou: writing – review & editing, funding acquisition, supervision, conceptualization.

Conflicts of interest

There are no conflicts to declare.

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